

Zeolite-microfragmenting Media: A Potential Strategy to Accelerate Coral Growth

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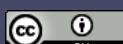
Abstract. Coral reef is an important underwater ecosystem which is rich in biodiversity in it. Coral growth has decreased drastically due to physical and chemical threats, such as the effect of warming seawater, fish bombing activities, and the effects of wastewater. The efficiency level of coral transplantation is determined by many factors, including the stability of the environment physical condition, the level of coral diversity, and the method of transplantation. The influence of the planting medium can also be a key factor in succeeding the coral transplantation process. The use of stable and natural growing media can be a solution to replace conventional growing media that have been used. Zeolite material is a medium that has many advantages such as amending the trace elemental contents of saltwater such as carbon absorbents, detoxifiers, ammonia remover, catalysts, promoting marine micro-algal growth, become a media for bacterial growth, etc. This review discusses the possibility of zeolites as the candidate media that can be used as a new medium in coral transplantation process to accelerate coral growth and maintain coral health by increasing the adaptation of corals to the effects of global climate change.

Keywords: Coral Growth, Microfragmentation, Transplantation, Zeolite.

1 Introduction

Coral reefs are one of the most vulnerable parts of marine ecosystems to climate change [1], where the increased of sea temperature, storm intensity, and ocean acidification effects contribute to the resilience and population of coral reef diversity in the world. Drastic climate change has triggered the rapid spread of mass coral bleaching [2]. In addition, the activities of coastal communities and the exploitation of fish that are not wise have resulted in sedimentation, eutrophication and water pollution. This directly changes the structure and function of coral reef ecosystems [3, 4], where the risk factors for species are high and are more susceptible to disease [5]. As a result, this population decline has a major effect on the resilience of marine ecosystems [6].

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2 Biology, Anatomy and Distribution of Corals

In general, reef-forming corals have mutually beneficial relationships with unicellular microscopic algae called zooxanthellae that lives in the gastrodermic cells of corals. As much as 90 percent of the organic material produced by algae is photosynthetically transferred to the host coral system. In addition to the symbiotic relationship with algae, most corals capture and eat live prey ranging from microscopic zooplankton to small fish, according to the size of coral. Using their tentacles protruding outside of their body, the coral uses the nematocytes or stinging cells to electrocute and kill its prey before it is brought into its mouth for digestion process. After the food is digested, the dregs of the digestive products are removed through the same hole.

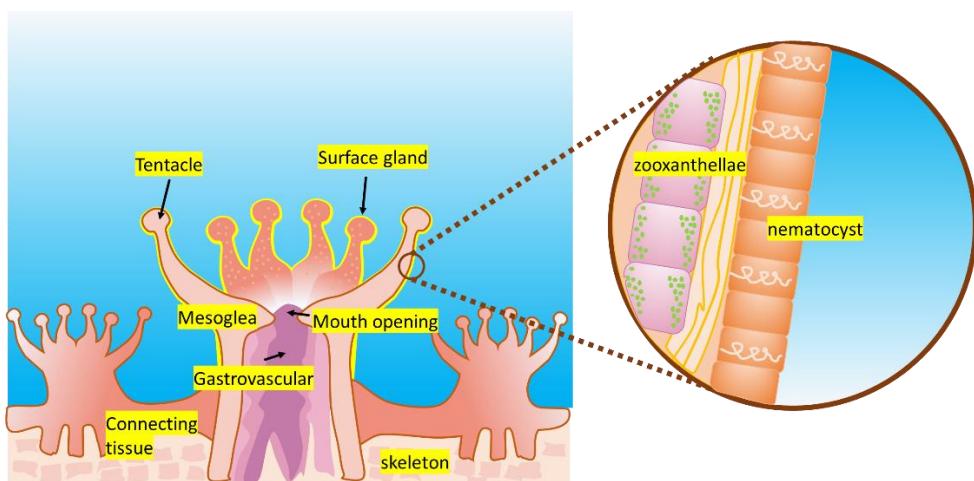


Figure 1. Schematic illustration of coral anatomy: coral polyps in symbiosis with zooxanthellae as a producer of oxygen supply for corals.

Corals are animals capable of reproducing both sexually and asexually. Coral sexual reproduction is a more common method and can be done in two ways namely natural spawning and artificial spawning. Sexual reproduction is carried out by corals by releasing sperm and eggs in the water column or in the stomach of their mother. Coral that releases eggs and sperm into the water column, fertilization occurs in the water column. Sexual reproduction is carried out by corals by releasing sperm and eggs in the water column or in the stomach of their parent. Coral that releases eggs and sperm into the water column, fertilization occurs in the water column. After the egg is fertilized by the sperm it will immediately develop into a free-swimming coral larva. Coral larvae vary in shape, generally shaped like a pear. When it is a larva, it does not have a chalk framework. Free swimming coral larvae will choose a hard substrate to attach to. After obtaining a suitable location for attaching the coral larvae metamorphose to form coral saplings and begin to produce limestone.

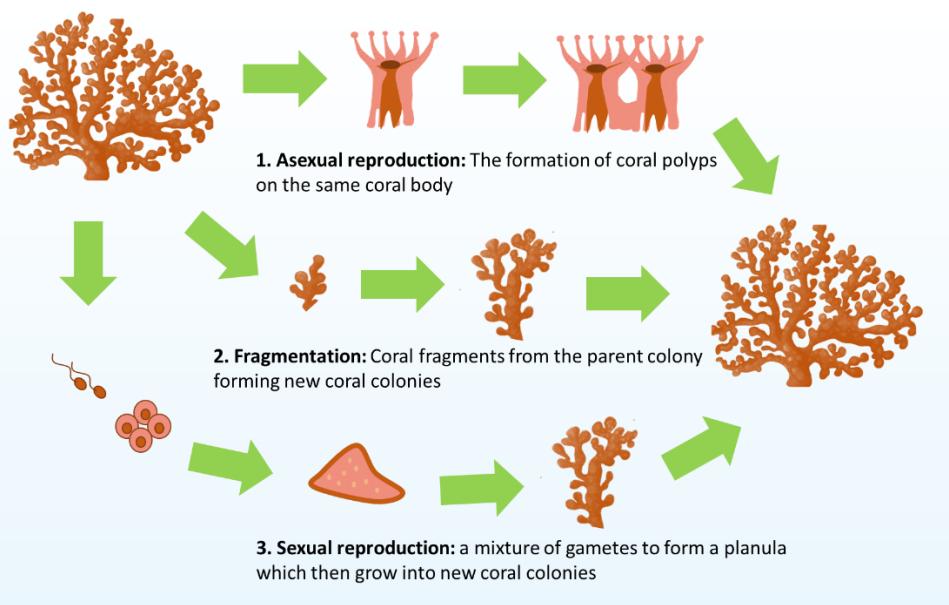


Figure 2. Schematic illustration of coral life cycle: 1. Asexually coral polyps split and grow into new coral polyps in the same colony; 2. coral fragments originating from fractures of the parent colony will form new colonies; 3. Male and female gametes meet and form planules which then grow into new coral colonies.

Location selection of the attachment is usually in a relatively protected place, because if it is attached to an open place it will be easily eaten by others biota. Artificial sexual reproduction is carried out by human assistance where the male gametes secreted by the corals are taken using special filters and released into the spawning pond. Artificial spawning is carried out to grow certain types of coral whose population is decreasing. Coral can be found in almost all marine waters in the world, from cold deep waters to shallow tropical waters. Shallow coral reefs have optimal growth rates in warm water ranging from 21.7–29.6 °C with salinity around 28.7-40.4 psu. The saturation state of coral aragonite is 2.82 with an average minimum light intensity of 450 $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$ [7]. More detailed information regarding coral condition can be seen in **Figure 3**. Coral reefs can be found at depths exceeding 91 m, but reef-forming corals generally grow best at depths shallower than 70 m. The most productive corals live at a depth of 18–27 m although in fact many of these shallow corals have been damaged. Corals need water with good salinity, which is around 25–45 ppt to survive, so it will be very difficult for corals to grow near river openings with low salinity. Other factors affecting the distribution of corals are the availability of a hard-bottom substrate, the availability of food such as plankton, and the presence of species that help control macroalgae, such as sea urchins and herbivorous fish.

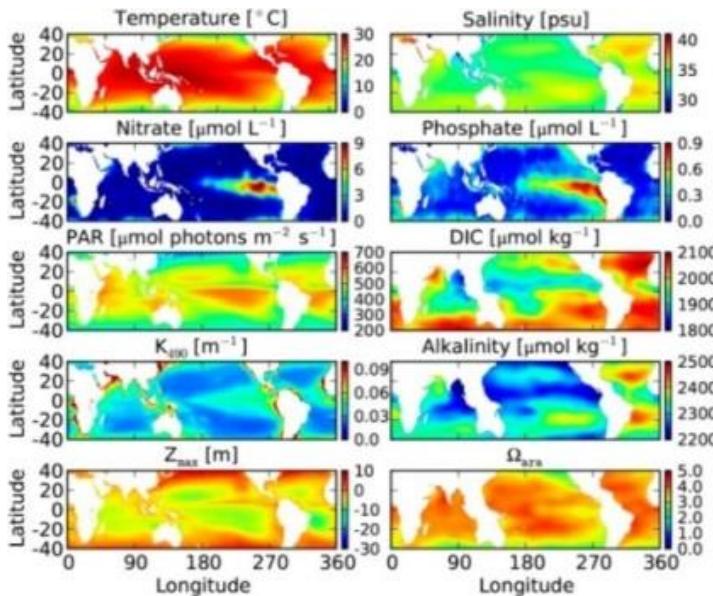


Figure 3. Calculation of temperature, salinity, and nutrient nutrition data. Data taken from [7].

One type of coral currently becomes a concern is the species of *Acropora* Spp coral. The genus *Acropora* are the most diverse reef-forming corals in the world [8]. This genus significantly contributes to island formation and coastal protection [9] because of their branching morphology, they are important habitats for other marine organisms [10] such as fish, turtles, echinoderms, crustaceans and mollusks [9]. Until now there are more than 149 species that have been reported on the World Register of Marine Species. The true number of species is unknown. This is due to the low inaccuracy of species validation due to complex cross-breeding between corals. *Acropora* species can grow as plates or slender branches or wide depending on the species and location. Like other corals, *Acropora* are colonies of individual polyps that are about 2 mm wide. Environmental parameters of coral growth and coral reef distribution depend on environmental conditions [12]. This conditions often change due to disturbances either from nature or human activities.

3 Diseases and Coral Reef Problems

Environmental damage has resulted a significant reduction in the population of *Acropora* and other coral species. When there is stress, *Acropora* is very susceptible to bleaching. Bleaching occurs due to loss of coral *zooxanthellae*, which give corals their color. Bleached coral is pale white and can die if new *Symbiodinium* cells are not able to assimilate to environmental conditions. Common things cause bleaching and coral mortality are pollution, unstable water temperatures, increased ocean acidification, sedimentation, and eutrophication. This makes coral population and species decreasing and threatened [13]. *Acropora* is a type of coral that is often used for the transplant method, which is a type of branching coral that grows fast enough to 8 cm/year. The results showed that this coral with an initial fragment length of 8 cm had a survival rate of 84%, an absolute growth of 0.8 cm and a growth rate of 0.021 cm/month [14]. Temperature, fragmentation size, sedimentation rate are inhibiting factors that can affect the survival of the transplanted *Acropora* and at a depth of 3 and 7 m the survival rate of *Acropora* corals is 70.83%, while on the control table the survival of transplanted corals is 66.67% [15].

In areas with strong and choppy currents, branching coral species cannot grow optimally [16], Acropora corals are branching corals. Meanwhile massive corals will grow predominantly on outer reefs with strong current conditions [17]. In reference [18] study, it was stated that smaller coral sizes tend to have a higher mortality rate than larger fragment sizes. Larger coral fragments have higher survival [19]. Acropora (branching) corals are very suitable to be used as coral fragments for transplantation activities because they have high survival rates and the growth is relatively fast [20].

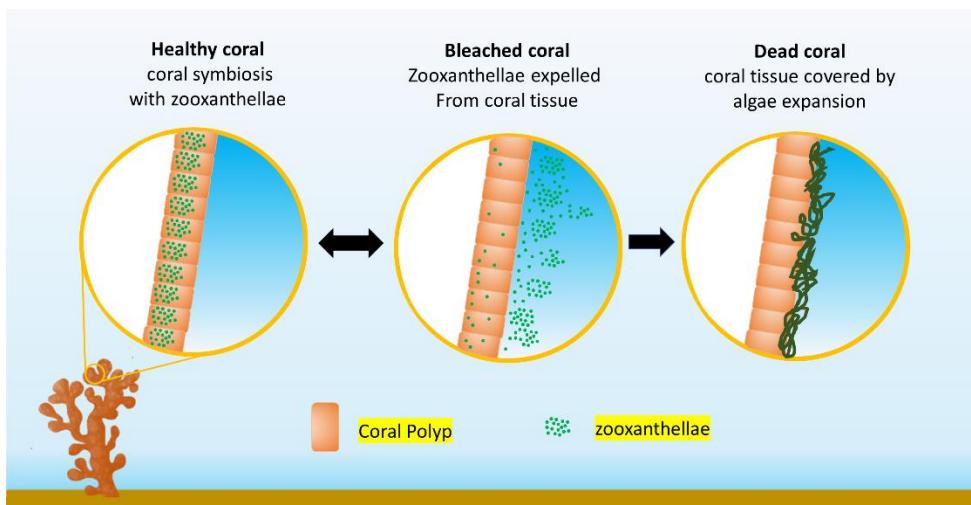


Figure 4. Illustrations of the coral bleaching process due to disease and significant weather changes.

The condition of coral reefs in the world is starting to decline. It is estimated that more than 20% of the world's coral has been damaged and shows no signs of repair. In Indonesia, the condition of coral reefs is very poor. In 2003, it was estimated that only 7% of Indonesia's corals were in very good condition, 27% were in moderate condition, and more than 36% were in poor condition [21]. The global decline of coral reefs is a well-documented phenomenon causing worldwide concern [22]. Threats to coral reefs can come from nature as well as threats from humans. Natural threats include: waves, storms, tsunamis and rising sea temperatures caused by climate change [23].

Some of the effects can be seen on the rate of metabolism, growth and reproduction, and changes to the outer shape of the coral so that it will affect the rate of coral growth which eventually accumulates seen in the percent of coral cover which describes the condition of coral reefs. However, humans are the most influential threat to coral reefs. Corals damaged by both natural and human factors are generally degraded to rubble [24, 25]. Live corals are scattered horizontally and vertically. The horizontal distribution of corals is limited by the presence of temperature and geographic location [24].

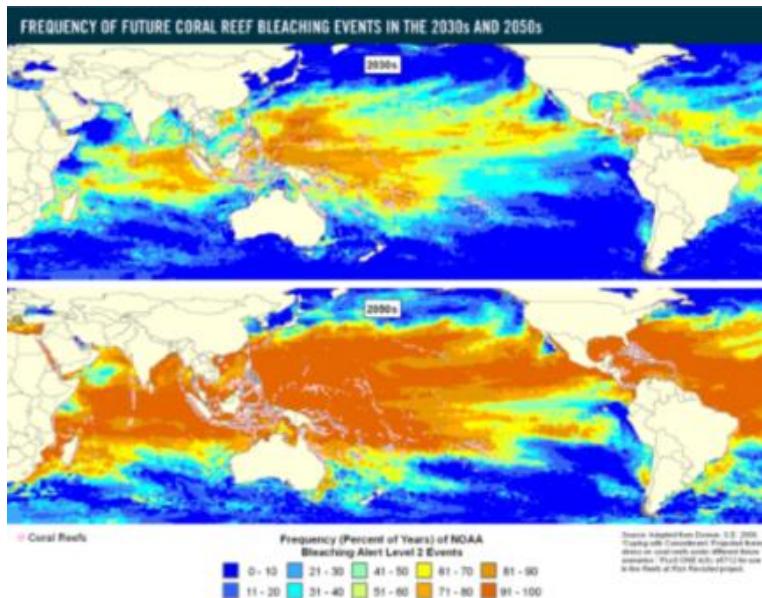


Figure 5. Map of coral bleaching conditions prediction [26]

4 Coral Restoration

Transplantation activity is one of the approaches that can be taken in order to restore damaged coral reef ecosystems as well as to improve ecological function. Transplantation activities in most cases are short-term and fail due to slow growth and reduced survival of coral fragments. There are many factors that cause this to happen, such as poor seedlings, water quality and unsuitable transplant locations, but the most influential thing is the unsuitable transplant model and the lack of post-transplant care, particularly for algae adherence. There are several types of coral that have been transplanted, including *Acropora* [27], *Pocillopora*, *Hypopora* sp, and *Sylopora* [28], *Plerogyra sinuosa*, *Euphyllia* sp, *Cynarina lacrymalis* [29, 30].

Several coral transplant methods that have been developed include the net and substrate rack method with the aim of facilitating installation and harvesting [29, 33], a concrete method to provide a solid substrate for transplanted corals and new coral larvae. [28, 31], nets and shards for easy access to materials [32], the natural substrate method [27], the biorock method using assistance from low-voltage electric currents [30], the tree method [34], and the hanging method to keep sediment away and provide room for growth [35, 36]. The stability of the physical condition of the environment, the level of coral diversity, and the method of transplantation are the determining factors for this transplantation process. One method that has been reported to be successful in assisting coral growth is the micro fragmentation technique [22]. Micro fragmentation is a process currently used as a method of reef restoration for coral reefs [37]. The planting medium can also be an important factor in the coral transplantation process. The use of corrosive media such as iron will interfere coral growth and also affect bacteria that are symbiotic with corals [38]. Likewise, plastic pipe media, in a long-term period it will break down into small, micro and even nano sized parts which have a very dangerous impact.



Figure 6. Coral micro fragmentation system in a laboratory scale transplantation process. This process can significantly increase coral growth [39]

Zeolites have been capable of stimulating the growth of the silicon-demanding marine micro-algae, like diatoms, mainly because they can act as a silicon buffer in seawater. Zeolites can also influence the yield of non-silicon-demanding algae because of the changes they can cause (liberation and adsorption of trace elements) in the composition of the media. The following competing factors have been identified as effects of zeolites on algal growth in saltwater: (i) ammonia decrease: growth inhibition reduced; (ii) macro-nutrients mainly silicon and bacterial activity are increase: stimulation of silicon-dependent algae; (iii) trace metals increase (desorption from zeolites) or decrease (adsorption): inhibition or stimulation, depending on the nature of the element and its concentration.

5 Zeolite Structure

Zeolites defined as crystalline inorganic polymers consisting of $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra, having the structure filled ions and water molecules, having great freedom of movement. Zeolites also defined as crystalline hydrated aluminosilicates of alkaline and earth-alkaline elements (particularly of sodium and calcium) such as in the figure 7 and figure 8. Zeolite is a group of crystalline microporous, aluminosilicate minerals with chemically neutral basic formed in a honeycomb-like structure. It is originated from volcanic rocks [40].

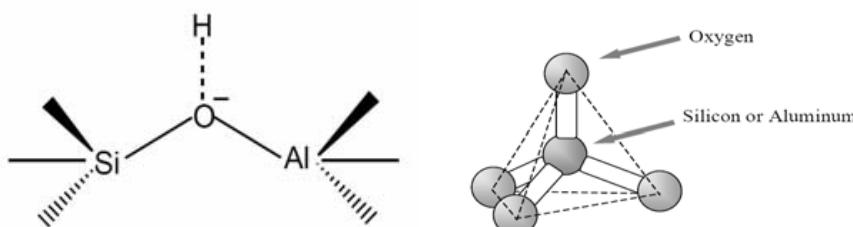


Figure 7. Primary building unit (PBU) of zeolite structure [40]

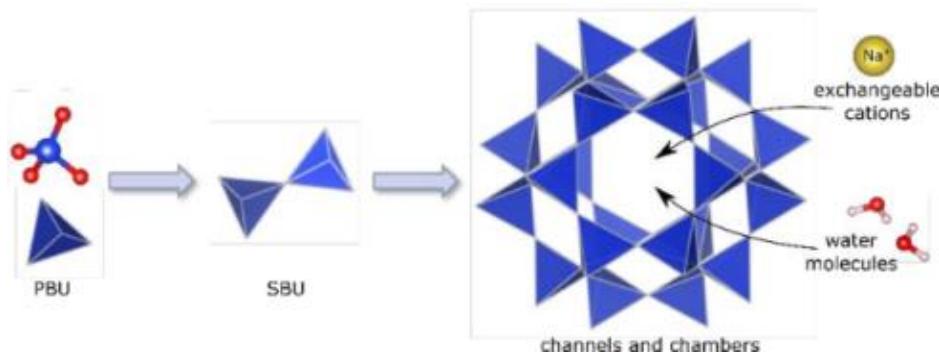


Figure 8. Scheme of zeolite structure (PBU = primary building unit, SBU secondary building unit) [41]

The specific structure of the zeolites gives them a number of unique properties, including low density and large volume of free spaces, shape-selectivity, possibility of sorption of molecules and ions, ion exchange capacity, catalytic properties etc. These properties make zeolites have large application as shown in the Figure 9. Zeolites have a high exchange capacity for cations in aquatic media. Their remarkably high cation-exchange capacity of up to 6 mmol (eq) per gram exceeds [42]. It has been shown that it is possible to modify zeolitic materials to make them powerful sorptive agents for many kinds of contaminants in aquatic systems [43]. The possibility of using zeolitic materials for media of coral transplantation bring many advantages such as adsorption of quous pollutants. However, competition of mono and divalent alkaline and alkaline-earth cations by the exchange sites at the zeolites surface limits the sorption capacity of heavy metals by zeolites in seawater when they are present in high concentrations.

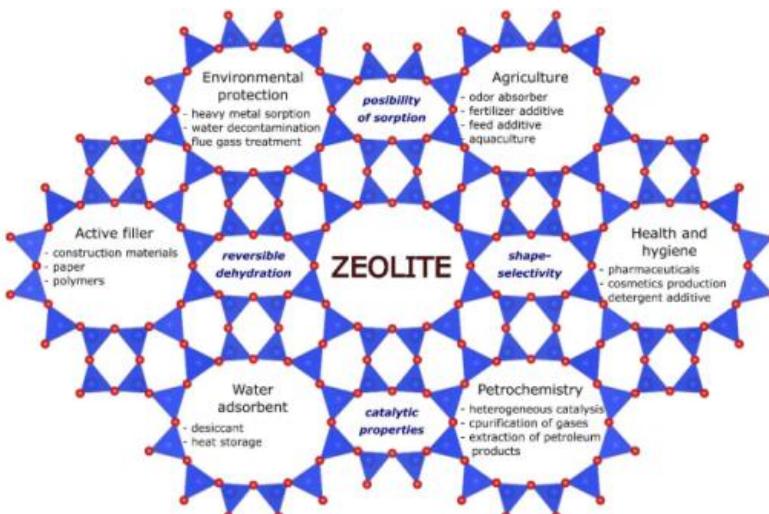


Figure 9. The wide range of Zeolite applications [41]

Figure 10 shows the unique structure of zeolites with high porosity (pore diameter 0.4-0.7 nm) allows efficient adsorption of wide range of charged elements such as ammonia, heavy metals, pesticides, smells, radioactive cations and many other toxins. One of the significant mechanisms involved in toxins uptake is known as Cation Exchange Capacity (CEC), which is defined as stoichiometric replacement of one equivalent of an ion in solid

phase by equivalent of another ion in liquid phase. Zeolites has CEC range 1.6-2.0 MEq/gm [44].

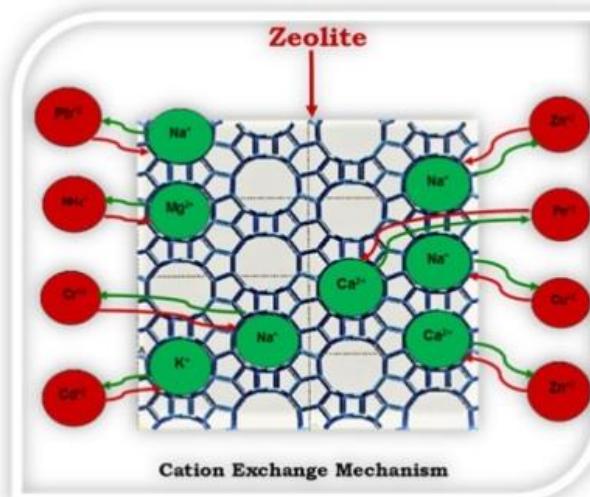


Figure 10. Cation exchange mechanism [45]

The reaction takes place between exchangeable cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) located in zeolite structure and cations (NH_4^+ , Cd^{2+} , Cu^{+2} , Hg^{+2} , Pb^{+2} , Cs^+ , Mn^+ , Rb^+ , Li^+ , Zn^{+2} , Fe^{+3} , Cr^{+3} , Co^{+3} , etc.) in solution. This ability known as, Molecular Sieves. When zeolite is saturated with cations, it should be reactivated though washing in clean salt water and reused many times before being 100% clogged. It was found that the loss of clinoptilolite capacity to be regenerated may occur after 10-11 regenerations [46].

The mechanism of zeolite works also showed in Figure 11 as an ion-exchange mechanism. The charge-balancing cations present on the raw zeolite surface (typically Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) can be replaced by another cation. The internal or zeolitic exchange sites potentially remain available to sorb smaller inorganic cations [44].

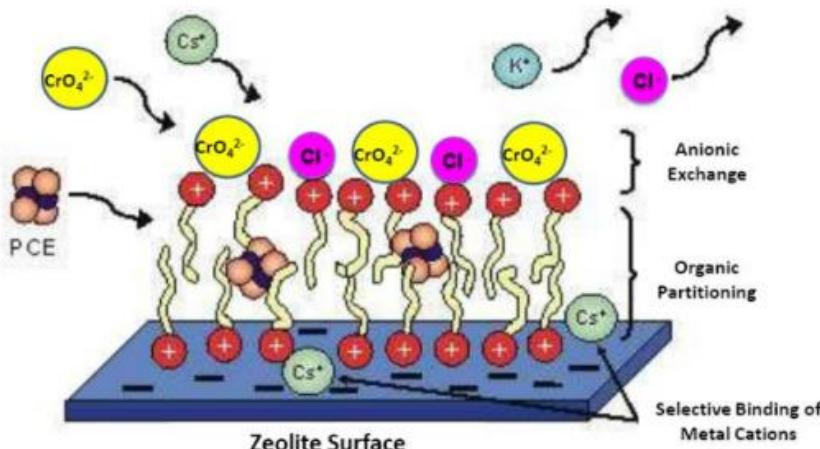


Figure 11. The mechanism of zeolite [44]

6 Important role of Zeolite

6.1 Improve Water Quality

Zeolite could be used to reduce or eliminate the content of ammonia, nitrite, hydrogen sulfide, heavy metals, and organic materials in fish ponds, increase the content of oxygen, adjust pH and minimize odors emitted from fish excretion. There are many factors affecting efficiency of zeolite, such as conductivity, pH, temperature and initial concentration of cations of the trade water, concentration and particle size of zeolite and exposure time. Zeolites has the highest efficiency and lowest cost compared to other materials such as activated carbon to reduce the content of ammonia in marine waters with efficiency exceeded 83% when the initial content of ammonia was 1.0ppm [47]. Reference [48] has conducted research about ammonia removal using zeolite in marine water. with initial concentration 3ppm, ammonia removal was 30 ppt. The effect of particle size of zeolites also has an effect. Decreasing zeolite particle size could improves the CEC and the capacity adsorption of ammonia. CEC was found to be 0.57 and 0.38meq NH4+/g zeolite for fine (1.00-0.125mm) and (2.00-1.00mm) sizes of clinoptilolite, respectively. Besides the particle size, how to put up zeolite water, greatly affect its efficiency in ammonia removal. [49] investigate that zeolite that was put inside a net bag reduced ammonia content in 72%, while zeolite that was put in aquarium diirectly reduced ammonia by 33% compared with control.

6.2 Heavy Metals Removal

Heavy metals removal efficiency from aqueous solutions using zeolite is affected by several factors, such as pH, temperature, presence of other contaminants in the treated water, properties of heavy metal ions, pre-treatment applied to zeolite, pore clogging, particle size, and zeolite purity [49]. Reference [51] investigated that the natural zeolite could remove different heavy metals from drinking water. Cadmium content (6ppm) in the rearing water of Mozambique tilapia could be reduced with removal efficiency 75% using zeolite at 4gm/litre.

6.3 Decrease Turbidity

Turbidity defined as content of suspended organic matter and total dissolved solids (TDS). Zeolite has the ability to decrease the turbidity. Reference [52] has conducted research in fish ponds, which certainly affect water quality, fish health and growth performance. It was found that ponds treated with zeolite resulted a decrease in total TDS from 635 to 400(mg/l), pH from 8.65 to 8.4, ammonia from 0.51 to 0.01ppm and better phytoplankton abundance. Even with zeolite incorporated in fish feed, water turbidity is diminished.

6.4 Enhancement of Diatom Growth

zeolites also claimed for its capability to improve micro-algae growth yields. *Chaetoceros* sp. growth was obtained in culture medium enriched with natural and artificial zeolites compared with non-enriched medium. zeolites promoted diatom growth as a result of zeolitic silicon leaching into seawater [53, 54]. Silicon atom inside the zeolite structure has been determined to be a limiting nutrient for diatom growth. Further experimental work found experimental evidence that some zeolites could also promote the growth of non-silicon-demanding microalgae, like flagellates. Despite the solubility of silica from the zeolitic structure being very low, a small fraction of hydrated silica. The ionization process at the seawater pH, and the ionic forms, such as $[\text{SiO}_3(\text{OH})]$, could took by diatoms equally with the non-ionic forms, such as orthosilicic, and $\text{Si}(\text{OH})_4$.

6.5 Decrease Hardness

Zeolites can purify and enhance the quality of the hard waters. Sodium ions exist in natural zeolite, can easily be loosed or replaced with other cations. Therefore, when hard water is passed through a bed of active granular zeolite, the sodium zeolite will be converted to calcium and magnesium zeolites. This means that water becomes free or less content of Ca^{2+} and Mg^{2+} (less hardness). Water hardness decreased significantly with values (328.4 to 42.4mg/L) together with the partial removal of Ca^{2+} and Mg^{2+} ions using natural zeolites [54].

6.6 Improve Fish Health

The indirect effects of applying zeolite is on the morphometrical index (growth performance and feed utilization) and Production index to better health index. The health index means better immunity status, less content of toxins in fish body, less deformities and pretty appearance. [50], conducted a research that Mozambique tilapia, exposed to high content of cadmium (6ppm) and treated with 4g zeolite/litre makes decrease of cadmium content in both water and fish flesh, an improvement in the total counts of red blood cells, platelets, and Hemoglobin, increase in RBC size, and decrease in white blood cells.

6.7 Biological filters

Zeolites are used in biological filters such as a substrate (media). The most important factors affecting the efficiency of biological filter is total surface area (TSA) which is the residence place for nitrifying bacteria, such as (*Nitrosomonas*, *Nitrobacter*, *Nitrococcus*, etc.). Nitrifying bacteria is responsible for converting harmful by-products (such as ammonia and nitrite) to more safe and beneficial by-product (nitrate). The greater TSA, the higher efficient nitrification process of biological filters [54]. Comparing the TSA of the common plastic media or sands used in biological filters with the TSA of zeolite of the same volume, we will discover that TSA for zeolite is hundred folds more than the previous medias. That leads to double the efficiency of biological filters. The addition of zeolites as a media in biological filter indicated removal of up to 80 % calcium, 89 % magnesium, 99 Iron, 56 % arsenic, 54 % fluorides, 96 % turbidity, 37% nitrates and 41% total organic carbon [56].

6.8 Chelating Agent for Micronutrients

Another advantage of using zeolite as a media for coral transplantation is an ability of the organic ligands of zeolites which strongly chelated micronutrients in seawater [57]. Since most organic ligands are directly, or indirectly produced by organisms, the nature of the biota can have a profound influence on metal speciation in aquatic systems. Investigation about metals-chelating organics have also been observed [58]. The amount of chelating organics released per cell (exudation) has also been influenced by organic ligand, probably due to the changes in the bioavailability of some of these trace elements. Therefore, in this review, we use Fe(III) as a dopping agent in the natural clinoptilolite.

7 Application of some zeolites in saltwater

7.1 Mordenite

Natural zeolites are hydrothermal and of mainly volcanic origin. They can occur both in crystallized forms found in igneous and trap metamorphic rocks, as well as insedimentary rocks. Ocean bottom sediments are relatively huge and rich is mordenite, a naturally occurring zeolite mineral that has vast range of applications especially in the adsorption of various pollutants like ammonium and heavy metals [59]. A side effect of the application of zeolites was the zeolites the chelating activity to two marine micro-algae species: a diatom (*Chaetoceros* sp.) and a haptophyte (*Isochrysis* sp.) which leads to feed the corals. Aparently by promoting the bacterium-mediated zeolites, coral transplantation will be accelerated.

stimulation in the growth of the marine micro-algae, particularly diatoms, used to feed the Fish [60]. Natural zeolites have a high selectivity for heavy metal ions and ammonium ions. However, due to their properties are strictly dependent on their crystal structure, natural zeolite has several limited applications. The main disadvantage is that the channel diameters are too small (such as clinoptilolite, which is the most common in nature, it is 0.30–4 nm), which do not allow for the adsorption of larger gas molecules and organic compounds. The need for the synthesis of molecular sieves and adsorbents with very specific parameters means that numerous attempts were made to obtain zeolites in the laboratory.

7.2 Modified Clinoptilolite-Fe(III)

Another zeolite that can be used as a transplantation media is modified Clinoptilolite-Fe(III). One of the ability and quality of zeolites is from ion exchange capabilities which expressed as the value of cation exchange capacity. The value of cation exchange capacity depends on the degree of substitution of the number of Al atoms which results in a negative charge on the zeolite framework. Although the capacity of zeolite adsorption capacity against large cations, natural zeolites do not show any affinity for anions [61].

The negative charge on the zeolite structure causes the zeolite to have a small ability to absorb the anion. One way of modifying zeolites to improve the anion exchange properties is by modification with transition metal cations, one of which is Fe(III). Ion Fe(III) can enter empty zeolite cavities and replace balancing cations in interchangeable zeolites. The modified zeolite with Fe(III) is no longer negatively charged because it has binds to Fe so it can be used to absorb the anions [62].

Chloride and bicarbonate is one of the causes of water hardness, whether it is permanent hardness. In industrial boilers (boiler, boil feed water), water is highly avoided because it will result in crust on the pipe/boiler, so its existence should be handled properly. Anion chloride and bicarbonate are present in ground water as soluble salts, both from cations derived from alkali metals, alkaline earths and transition metals [63]. Therefore, to enhance the capability of eliminating those ions, the Fe(III) ions should be doped onto a clinoptilolite.

7.3 Zeolite-A

Zeolite A is of great industrial importance due to its molecular sieving, ion exchange and water adsorption properties. With the molar ratio Si/Al nearly equal to one, kaolin is an ideal raw material for preparing NaA zeolite. Kaolin was one of the most versatile industrial minerals and was used extensively for many applications, especially for adsorbing heavy metals as well as for adsorbing CO₂ level in the sea water.

Seawater absorbs CO₂ to produce carbonic acid (H₂CO₃), bicarbonate (HCO⁻) and carbonate ions (CO₃)²⁻ levels lead to increases in the concentration of carbonic acid and bicarbonate ions, causing a decrease in the concentration of carbonate ions and a resultant reduction in calcification rates. This means that increases in CO can cause decreases in the growth rates of corals (and other calcareous organisms) and weaken their skeletons. Their ability to compete for space on the reef is reduced and they become more susceptible to breakage and bio-erosion. If calcium carbonate removal exceeds the calcification rate, reefs can shrink in size [64]. Therefore, the use of zeolite A hopefully could reduce the CO₂ level in the sea.

8 Conclusion

The need for coral repair caused by various things, whether caused by humans or nature because of the various benefits of corals that have a major impact on the ecosystem in the ocean. Seeing the content possessed by zeolites, it is expected to help in coral growth and preservation. Clinoptilolite-Fe(III) (NZ-Fe), Mordenite (M), and Zeolite A are three types of potential zeolites which can be used as a micro fragmenting media for coral transplantation. Zeolites have many advantages such as amending the trace elemental contents of saltwater such as NO_3 , promoting marine micro-algal growth, become a media for bacterial growth, the application of zeolites in saltwater, the role of Fe on the bacterial growth, the role of zeolites on cultures of micro-algae, the role of organically chelated trace, etc. From the content and the properties possessed by zeolites, it is assumed that the use of this zeolite mineral can be used as a substrate for attaching seeds to coral reefs. However, There are several factors that affect the efficiency of zeolite, : (1) initial metal concentration in seawater; (2) levels of trace metals in the zeolites (contaminants); (3) characteristics of the zeolites in terms of both ion-exchange capacity and specific affinities for the different cations; (4) quantity of zeolite per liter of solution; (5) pH (6) response of the organism in terms of liberation of organic ligands and (7) the acceleration of coral growth using different zeolite media. Summary, the micro fragmentation method, zeolite can be used as a natural growth medium. Therefore, this article can be used as a reference for further research.

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